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XX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON SOME NITRO DERIVATIVES OF METABROMTOLUOL.

By W. B. Bentley and W. H. Warren.

Presented May 28, 1889.

Determination of the Constitution of Metabromdinitrotoluol, $C_6H_2CH_3Br(NO_2)_2$.

Our attention was first called to this subject by Prof. C. Loring Jackson, who, having with W. S. Robinson* obtained the metabromdinitrotoluol by the decomposition of their bromdinitrophenylmalonic ester, asked us to determine its constitution.

This metabromdinitrotoluol, melting point 103°–104°, was discovered by Grete,† who made it by the action of fuming nitric acid on metabromtoluol, or metabrommononitrotoluol, and assigned to it the constitution CH_3, NO_2, Br, NO_2, 1, 2, 3, 4, although he was very doubtful about the position of the second nitro group, giving it the para position without any experimental reason for doing so. His proof that one of the nitro groups was in the ortho position consisted in establishing the identity of the bromtoluidine made by the reduction of his bromnitrotoluol with that obtained by the action of bromine on orthoacettoluid; ‡ but this obviously leaves it doubtful whether this nitro group stands in the position 2 or 6 to the methyl of the toluol, and in fact later work has shown that Grete was wrong in ascribing to it the position 2, as his mononitro compound really has the constitution CH_3, Br, NO_2, 1, 3, 6. The proof of this was given by Nevile and Winther,§ who, by replacing the amido group in the metabromorthotoluidine (melting point 55°–56°) already mentioned by bromine, obtained a liquid dibromtoluol, which on oxidation with nitric acid yielded the dibrombenzoic acid melting at 151°–153° previously made by Von Richter[*] from paradibrombenzol.

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* See preceding paper.

† Ann. Chem., clxxvii. 258.

‡ Wroblewsky, Ann. Chem., clxviii. 161.

§ Ber. d. ch. G., xiii. 962.

The only point therefore not settled in regard to the constitution of Grete's metabromdinitrotoluol was the position of the second nitro group, which might be either para or ortho to the methyl. To determine this the metabromdinitrotoluol was heated with alcoholic ammonia[†] in sealed tubes to 100° for 12 hours, when it was found to be converted into a yellow substance, which had partly separated in the solid state, and partly remained in solution in the alcohol, from which it was obtained by evaporation. The product was purified by washing with water to remove the ammonic bromide, and crystallization from hot glacial acetic acid, until it showed a constant melting point (193°–194°), when it was dried at 135°, and the following analysis showed that a dinitrometatoluidine had been formed.

0.2658 gr. of the substance gave 51.2 c.c. of nitrogen at a temperature of 24° and a pressure of 767.5 mm.

	Calculated for $C_6H_2CH_3NH_2(NO_2)_2$.	Found.
Nitrogen	21.31	21.71

The melting point showed that this substance is identical with the dinitrotoluidine made by Hepp[‡] by the action of alcoholic ammonia on his γ trinitrotoluol, but the constitution of this trinitrotoluol had not been determined. Staedel[§] has also announced recently that one of his students, Herr Adalbert Kolb, has prepared a dinitrotoluidine from dinitrokresolether and determined its constitution as CH_3, NH_2, NO_2, NO_2, 1, 3, 4, 6; but, as he neglected to give the melting point, we were unable to tell whether it was identical with ours or not, and have been forced to work out the constitution of our dinitrotoluidine by the replacement of the amido group by hydrogen. In doing this some difficulty was encountered because of the very slight solubility of the dinitrotoluidine in alcohol, but we found on experiment that the Griess reaction would take place satisfactorily in a mixture of acetone and alcohol, and accordingly proceeded as follows. 2 grs. of the dinitrotoluidine were dissolved in about 12 c.c. of acetone, 8 c.c. of common alcohol added, and the mixture acidified with strong sulphuric acid, after which 1.5 grs. of sodic nitrite, about twice the calculated amount, was added in small portions at a time, and the liquid warmed gently until the evolution of nitrogen ceased, when the larger part of the acetone and alcohol was distilled off at first on the water bath, finally on the sand bath, and the residue distilled with steam; the dinitrotoluol passed over into the receiver in small white crystals, which were removed by filtration, and crystallized from hot alcohol until they showed the constant melting point 71°. It was not worth while to dilute the distillate of acetone and alcohol, as no precipitate was obtained in that way. For greater certainty the product was analyzed, with the following results: —

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[*] Ber. d. ch. G., vii. 1146.

[†] When metabromdinitrotoluol was allowed to stand with alcoholic ammonia in the cold, a dark blue solution was formed at first, but the color gradually changed to reddish brown.

[‡] Ann. Chem., ccxv. 371.

[§] Ber. d. ch. G., xxii. 215.

0.2456 gr. of the substance gave 33.1 c.c. of nitrogen at a temperature of 22° and a pressure of 764.2 mm.

	Calculated for $C_6H_3CH_3(NO_2)_2$.	Found.
Nitrogen	21.31	21.71

There is no question therefore that the substance is the orthoparadinitrotoluol, CH_3, NO_2, NO_2, 1, 2, 4, and the bromdinitrotoluol accordingly has the following constitution: CH_3, Br, NO_2, NO_2, 1, 3, 4, 6. It follows also that our dinitrotoluidine is identical with that described by Kolb, and, if Staedel had given its melting point, it would not have been necessary for us to determine its constitution. As has been already stated, this dinitrotoluidine melts at the same point as that made by Hepp from alcoholic ammonia and his γ trinitrotoluol. To establish the relation between these substances more firmly, we made the dinitrophenyltoluidine by treating our dinitrobromtoluol with aniline, and found that the product showed the same melting point, 142°, as that of the compound made by Hepp from γ trinitrotoluol and aniline. The γ trinitrotoluol of Hepp therefore has the following constitution: CH_3, NO_2, NO_2, NO_2, 1, 3, 4, 6; which is in harmony with Laubenheimer's rule,* that a nitro group is removed by the action of alcoholic ammonia only when it is in the ortho position to another nitro group.

Metabromtrinitrotoluol, $C_6HCH_3Br(NO_2)_3$.

In preparing the metabromdinitrotoluol, we found, if a mixture of fuming nitric acid and sulphuric acid was used, that a new substance melting above 104° was obtained, which turned out to be the as yet undescribed metabromtrinitrotoluol. This compound is most easily prepared from the metabromdinitrotoluol, when it is convenient to proceed as follows. 5 to 10 grs. of metabromdinitrotoluol were placed in a flask, and 10 to 20 c.c. of a mixture of two volumes of fuming nitric acid and one of strong sulphuric acid added. The whole was then boiled until the evolution of red fumes had nearly ceased, when, after it was cool, it was poured in a fine stream into a beaker of cold water, stirring the liquid vigorously during the addition of the acid solution, as in this way the product is precipitated in a granular form much more easy to manage than the large compact lumps obtained if the stirring is neglected. The product was then washed with cold water till free from acid, and purified by crystallization from alcohol, until it showed the constant melting point 143°. The residue from the mother liquors, consisting of a mixture of metabromtrinitrotoluol and the corresponding dinitro compound, can be advantageously used for preparing a fresh quantity of the trinitro body. The pure substance was dried at 120°, and analyzed with the following results:—

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* Ber. d. ch. G., ix. 766, 1828.

I. 0.3372 gr. of the substance gave on combustion 0.3356 gr. of carbonic dioxide and 0.0453 gr. of water.

II. 0.2651 gr. of the substance gave 32.9 c.c. of nitrogen at a temperature of 21° and a pressure of 761.5 mm.

III. 0.1830 gr. of the substance gave, by the method of Carius, 0.1120 gr. of argentic bromide.

	Calculated for $C_6HCH_3Br(NO_2)_3$.		Found.	
		I.	II.	III.
Carbon	27.46	27.14		
Hydrogen	1.31	1.49		
Nitrogen	26.14		26.04	
Bromine	13.73			14.09

The yield was about 60 per cent of the theoretical.

Properties.—The metabromtrinitrotoluol crystallizes from alcohol in small white needles, which melt at 143°. They are insoluble in water, or ligroine; nearly insoluble in cold alcohol, only sparingly soluble in hot; slightly soluble in carbonic disulphide; soluble in ether, methyl alcohol, benzol, chloroform, glacial acetic acid, or acetone. Boiling alcohol we found the best solvent for it, although it is so slightly soluble in it. Aqueous sodic hydrate seemed to have no action upon it, nor was it affected by the strong acids. The bromine is removed easily, which we proved by the action of alcoholic ammonia or aniline on it, as will be described later in this paper.

Constitution of Metabromtrinitrotoluol.

As the metabromtrinitrotoluol is made from the metabromdinitrotoluol, the only point to be determined is the position of the third nitro group; for this purpose we converted it into the corresponding trinitrotoluidine by treatment with alcoholic ammonia in the cold. The mixture was allowed to stand in a corked flask for about twelve hours; at first a dark blue color appeared in the liquid, but on longer standing this turned to a deep reddish brown, and a precipitate was deposited, which with the supernatant liquid at the end of the twelve hours was poured into a dish, and the solvent allowed to evaporate spontaneously. The residue, which was red and yellow, was washed till free from ammonic bromide, and then purified by crystallization from hot glacial acetic acid, until it showed the constant melting point 136°, when it was dried at 120°, and analyzed with the following result: —

0.1144 gr. of the substance gave 24.2 c.c. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

	Calculated for $C_6HCH_3NH_2(NO_2)_3$.	Found.
Nitrogen	23.14	23.51

The melting point of this trinitrotoluidine shows that it is identical with that prepared by Nölting and Salis[*] by the action of alcoholic ammonia on trinitrometakresolethylether, to which they assign the constitution CH_3, NO_2, NH_2, NO_2, NO_2, 1, 2, 3, 4, 6, on the ground that the alcoholic ammonia did not remove any of the nitro groups, and therefore, according to Laubenheimer,[†] no two of them could be in the ortho position to each other, and this is the only possible arrangement in which no two nitro groups are in the ortho position. Our metabromtrinitrotoluol must consequently have the constitution CH_3, NO_2, Br, NO_2, NO_2, 1, 2, 3, 4, 6; and this conclusion is confirmed by the fact recently discovered in this laboratory,[‡] that the bromtrinitrophenylmalonic ester is converted by boiling with sulphuric acid of specific gravity 1.44 into this metabromtrinitrotoluol melting at 143°. As the bromtrinitrophenylmalonic ester is made from the symmetrical tribromtrinitrobenzol, Br, NO_2, Br, NO_2, Br, NO_2, 1, 2, 3, 4, 5, 6, it can have only the constitution $CH(COOC_2H_5)_2$, NO_2, Br, NO_2, NO_2,

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[*] Ber d. ch. G., xv. 1864.

[†] Ber. d. ch. G., ix. 766, 1828.

[‡] C. Loring Jackson and G. D. Moore. These Proceedings, xxiv. 268.

1, 2, 3, 4, 6, which leads to the constitution of our metabromtrinitrotoluol given above.

Anilidotrinitrotoluol, $C_6HCH_3(C_6H_5NH)(NO_2)_3$.

This substance was prepared by treating metabromtrinitrotoluol with aniline in the proportion of two molecules of the base to one of the nitro compound; the action is violent, accompanied with considerable evolution of heat, and the product was easily purified by crystallization from a mixture of alcohol and benzol, until it showed the constant melting point 151°, when it was dried at 120°, and analyzed with the following results: —

I. 0.2804 gr. of the substance gave on combustion 0.5031 gr. of carbonic dioxide and 0.0936 gr. of water.

II. 0.2777 gr. of the substance gave 43.2 c.c. of nitrogen at a temperature of 27°.5 and a pressure of 772 mm.

	Calculated for $C_6HCH_3(C_6H_5NH)(NO_2)_3$.	Found.	
		I.	II.
Carbon	49.06	49.03	
Hydrogen	3.14	3.71	
Nitrogen	17.61		17.41

Properties. — The metanilidotrinitrotoluol crystallizes from a mixture of alcohol and benzol in well developed shining yellow plates, which melt at 151°. The substance is insoluble in water or ligroine; sparingly soluble in ethyl or methyl alcohol; soluble in ether, chloroform, benzol, carbonic disulphide, glacial acetic acid, or acetone. The most convenient solvent for it is a mixture of five parts of alcohol with one of benzol. Aqueous sodic hydrate dissolves it with a red color, and hydrochloric acid throws down from this solution the original substance apparently unaltered. Strong sulphuric or strong nitric acid dissolves it, but strong hydrochloric acid does not.

The constitution of this substance is CH_3, NO_2, C_6H_5NH, NO_2, NO_2, 1, 2, 3, 4, 6, as is shown by its preparation from the metabromtrinitrotoluol, the constitution of which has been determined, as given earlier in this paper.